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(21) International Application Number: PCT/EP91/02014 (22) International Filing Date: 23 October 1991 (23.10.91) (30) Priority data: 604,708 25 October 1990 (25.10.90) US (71) Applicant (for AT only): SANDOZ-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT M.B.H. [AT/AT]; Brunner Strasse 59, A-1235 Vienna (AT). (71) Applicant (for DE only): SANDOZ-PATENT-GMBH [DE/ DE]; Humboldtstrasse 3, D-7850 Lörrach (DE). (71) Applicant (for all designated States except AT DE): SAN- DOZ LTD. [CH/CH]; Lichtstrasse 35, CH-4002 Basle (CH).		(72) Inventor: LEE, Shy-Fuh ; 228 Carbonera Avenue, Sunny- vale, CA 94086 (US). (74) Agent: SANDOZ LTD.; Lichtstrasse 35, CH-4002 Basle (CH). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CA, CH (European patent), CS, DE (European patent), DK (European patent), ES (Euro- pean patent), FR (European patent), GB (European pa- tent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), PL, SE (European patent), SU ⁺ . Published <i>With international search report.</i>
(54) Title: HETEROCYCLIC DIONE DERIVATIVES AS PESTICIDES AND PLANT GROWTH REGULATORS (57) Abstract The present invention concerns substituted 3,5-dioxo-3,4,5,6-tetrahydrooxazines as herbicides, processes and intermediates for their preparation, compositions containing them and their use as herbicides and acaricides.		

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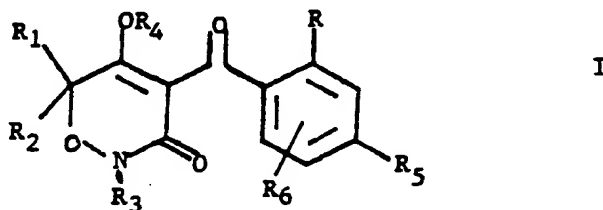
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HETEROCYCLIC DIONE DERIVATIVES AS PESTICIDES AND
PLANT GROWTH REGULATORS

The present invention concerns substituted 3,5-dioxo-3,4,5,6-tetrahydrooxazines as herbicides, processes and intermediates for their preparation, compositions containing them and their use as herbicides and acaricides.

USP 4,695,673 describes a wide range of acylated 1,3-dicarbonyl compounds and their use as herbicides but makes no reference to or suggestion of the 3,5-dioxotetrahydrooxazine ring characterizing the compounds of the present invention.

More particularly, the invention concerns compounds of formula I



wherein,

each of R_1 , R_2 and R_3 is independently hydrogen, C_{1-8} alkyl, carboxyl, C_{1-8} alkoxycarbonyl, phenyl or phenyl substituted by one to three groups as R, or R_1 and R_2 together form a C_{3-6} alkylene bridge

R_4 is hydrogen, C_{1-8} alkyl, C_{1-8} alkylcarbonyl, C_{1-8} alkoxycarbonyl, $-C(O)NR_7R_8$, C_{1-8} alkylsulphonyl, $P(O)-(OR_9)_2$, $R_7P(O)-OR_9$, benzoyl or a cation.

R is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkoxy optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkylcarbonyl, C_{1-8} alkoxycarbonyl, NR_7R_8 , $O_nS(O)_n \cdot R_{10}$, $NR_7SO_2R_8$, halogen, cyano or nitro.

R_5 is C_{1-8} alkoxy substituted by 1 to 6 halogen atoms;

R_6 is hydrogen or selected from the meanings given for R;

each of R_7 and R_8 is independently hydrogen or C_{1-8} alkyl;

R_9 is C_{1-8} alkyl;

R_{10} is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms;

n is 0 or 1;

n' is 0, 1 or 2;

provided that when R_1 , R_2 and R_3 are methyl, R_4 and R_6 are hydrogen and

R is nitro, R_3 is not difluoromethoxy.

In the above definitions, halogen is conveniently selected from chloro, bromo and fluoro, C_{1-8} alkyl moieties, preferably have 1 to 4 carbon atoms.

Each of R_1 , R_2 and R_3 is preferably hydrogen, C_{1-4} alkyl especially hydrogen or C_{1-3} alkyl.

R conveniently signifies C_{1-4} alkyl optionally substituted with

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halogen, $-(O)_n-S(O)_n-C_{1-4}alkyl$, halogen or nitro. It is preferably methyl, CF_3 , $C_{1-3}alkylsulfonyl$, $C_{1-3}alkylsulfonyloxy$, chloro, bromo or nitro.

R_5 is preferably fluoroalkoxy, more preferably OCF_3 .

R_6 is preferably hydrogen, $C_{1-4}alkyl$, $C_{1-4}alkoxy$, bromo, chloro; it is more preferably hydrogen, methoxy or chloro.

R_4 is conveniently hydrogen, $C_{1-4}alkyl$, $C_{4-8}alkylcarbonyl$, benzoyl, $C_{1-4}alkylsulfonyl$ or a cation. It is preferably hydrogen, methyl, ethyl, t-butylcarbonyl, isobutylcarbonyl, benzoyl or methylsulfonyl. As a cation R_4 is preferably an alkali metal such as Na^+ , K^+ , Li^+ or an ammonium cation.

Examples of particularly preferred substituents are for R_1 and R_2 each
 - a) H, $C_{1-4}alkyl$, phenyl or phenyl substituted by one to three groups as R

b) H, $C_{1-4}alkyl$ phenyl or phenyl substituted by one to three groups as R

c) H, $C_{1-3}alkyl$

d) H, CH_3

e) $C_{1-3}alkyl$

R_3 - a) $C_{1-8}alkyl$

b) $C_{1-4}alkyl$

c) CH_3 , C_2H_5

R_4 - H

R - a) NO_2 , Cl, CF_3

b) NO_2 , Cl

c) NO_2

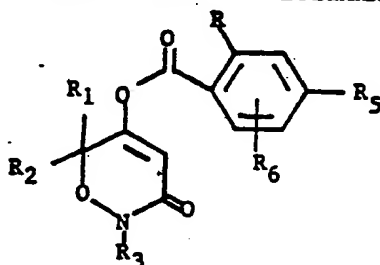
R_5 - OCF_3

R_6 - H

Combinations of these substituent meanings are especially preferred.

A particularly preferred single compound is 2,6,6-trimethyl-4-(4-trifluoromethoxy-2-nitrobenzyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione.

The compounds of the present invention of formula I are new substances which can be prepared by methods analogous to methods known in the art, such as those described in European Patent Application EP 186,117 and references cited therein. More particularly, they can be obtained by, for example: rearranging an enol ester of formula (II)



II

wherein R_1 , R_2 , R_3 , R, R_5 and R_6 are as previously defined to give a compound of formula I wherein R_4 - H.

This rearrangement is conveniently effected by reacting the compound

of formula II with a cyanide source and a moderate base.

For example, the reaction may be carried out in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base. The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. 1,2-dichloroethane, toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide (DMF) and methyl isobutyl ketone (MIBK). In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 80°C. In some cases, for instance when there is a possible problem of excessive by-product formation, the temperatures should be kept at about 40°C maximum.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C₂-C₃ aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin. The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. Generally about 1-10 mole % of the cyanide source is preferred.

By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this reaction include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate. The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 1.3-2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

Compounds of formula I where R₄ is other than hydrogen can be prepared by reacting a compound of formula I wherein R₄ is hydrogen with either

a) the group R₄₀-OH and a catalyst, or

b) the group R₄₀-Q and a moderate base, wherein Q is a halogen atom, to give a compound of formula I where R₄₀ is the desired substituent.

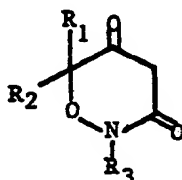
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The above reaction a) is carried out in the presence of a catalyst such as concentrated sulfuric acid. The reaction is conveniently carried out in a solvent which is also the reactant such as methanol, and at an elevated temperature.

5 The above reaction b) is carried out in the presence of a moderate base such as triethylamine or pyridine and conveniently at RT or below.

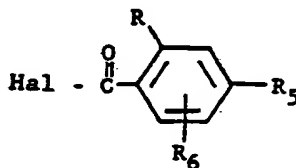
The compounds of formula I may be recovered from the reaction mixture in which they are formed by working up by established procedures.

10 The compounds of formula II may be prepared by reacting a compound of formula III



III

15 with a compound of formula IV



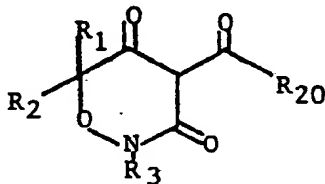
IV

20 This reaction is carried out in the presence of a base such as triethylamine, potassium carbonate, pyridine, preferably triethylamine and in an inert solvent such as dichloromethane, acetonitrile, toluene, tetrahydrofuran, dimethylformamide. The reaction is conveniently carried out at RT or below.

25 The remaining compounds of formula II may be prepared analogously.

The compounds of formula III are new and also form part of the invention.

30 They may be prepared by decarboxylating a compound of formula V

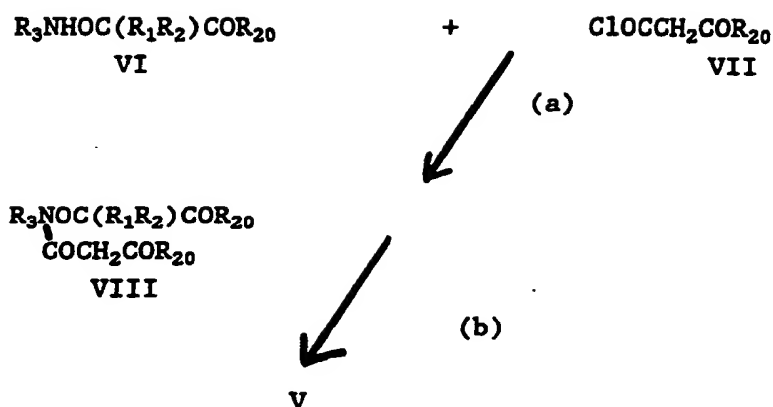


V

35 wherein R₂₀ is alkoxy, especially ethoxy or methoxy and R₁, R₂ and R₃ are as defined above. The reaction may be carried out at elevated temperatures e.g. 80-90° and in an inert solvent such as e.g. wet dimethylsulfoxide.

40 The compounds of formula V may be prepared analogously to known methods e.g. according to the following reaction scheme.

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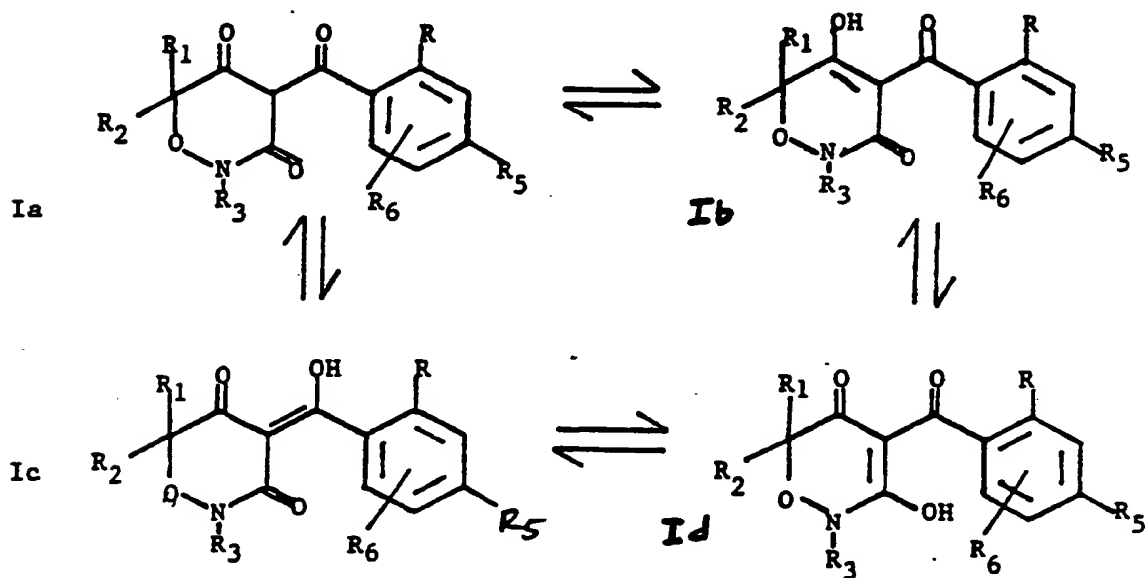
Reaction (a) may be carried out in an inert solvent such as dichloromethane and aqueous ether and in the presence of a base such as triethylamine or sodium carbonate at RT.

Reaction (b) may be carried out in an inert solvent such as toluene benzene or tetrahydrofuran in the presence of a base such as sodium methoxide or sodium hydride.

The remaining starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the processes described herein or to known processes [cf for compounds VI Kornowski et.al. Bull. Soc. Chim France 1966(2)683].

The compound 2-nitro-4-trifluoromethoxy-benzoic acid is new and also forms part of the invention.

The compounds of this invention wherein R_4 is H can have four structural formulae because of tautomerism as illustrated as follows:



6

It will of course be readily appreciated that where R_4 is other than hydrogen such compounds may exist in forms Ib, Ic and Id or as mixtures of these forms.

The novel compounds of formula I are useful for the control of weeds, using pre- and/or post-emergent treatments. Compounds of formula I are also useful as plant growth regulators (PGRs) and acaricides. The compounds can be applied in the form of dusts, granules, solutions, emulsions, wettable powders, flowables and suspensions. Application of a compound of the present invention as herbicides is made according to conventional procedure to the weeds or their locus using an herbicidally effective amount of the compounds, usually from about one-tenth or less to ten pounds per acre. The application of a compound of the present invention to the "locus" of the weed includes application to the seeds, the plant (weed) or parts of the plant, or the soil.

Application of a compound of the present invention as an acaricide is made according to conventional procedure to the site of infestation using an acaricidally effective amount of the compound, usually 100 g/ha to 1 kg/ha.

The term "herbicide," as used herein, refers to an active ingredient which modifies the growth of plants because of phytotoxic or plant growth regulating properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

Compounds of the present invention, when applied as either post or pre-emergents, demonstrate high levels of herbicidal activity on broadleaf, grass and sedge weeds. They also exhibit selectivity in wheat, corn, cotton, some varieties of soybean and in some cases, rice.

In the use of the compounds of formula I for combatting weeds and acari, a compound of formula I, or mixtures thereof, can conveniently be employed as compositions in association with acceptable diluent(s) for application to the weed, acari or their loci. Such compositions also form part of the present invention.

Methods of preparing suitable formulations which can be used with a compound of the present invention are described in the literature along with suitable liquid and solid carriers, such as in U.S. Patent 4,192,669 and 4,163,661, which are incorporated herein by reference. The optimum usage of a compound of the present invention is readily determinable by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot testing.

Suitable formulations contain from 0.01 to 99% by weight of active ingredient, from 0 to 20% of surfactant and from 1 to 99.99% of solid or liquid diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of a composition generally contain between 0.01 and 25% by weight of active ingredient. Lower or higher

levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90%, preferably between 5 and 81% by weight of active ingredient.

Useful formulations of the compounds of formula I include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula I with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula I may be used in micro-encapsulated form.

The compounds of formula I can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the weed, acari or their loci.

Agriculturally acceptable additives may be employed in the herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such as xylene or an alcohol such as isopropanol, and for liquid application forms e.g. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary acaricidal or herbicidal activity for broadspectrum weed control or compounds having antidotal, fungicidal, insecticidal or insect attractant activity.

The following examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight.

EXAMPLE 1

Preparation of 2,6,6-trimethyl-4-(2-nitro-4-trifluoromethoxybenzoyl)-2H-1,2-oxazine-3,5(4H, 6H)-dione (Formula I $R_1-R_2-R_3=CH_3$; $R_4-R_5=H$; $R=NO_2$; $R_6=OCF_3$; Compound No. 1)

71.4 g of 2,6,6-trimethyl-5-(2-nitro-4-trifluoromethoxybenzoyloxy)-6H-1,2-oxazine-3-one is dissolved in 300 ml of acetonitrile and 49 ml of triethylamine. To this solution, cooled in a water bath, is added 3.2 ml of acetone cyanohydrin. The resulting solution is stirred at r.t., under nitrogen, overnight. The reaction mixture is concentrated to a syrup and the syrup is portioned between 400 ml of water and 150 ml of dichloromethoxy. The combined extracts are washed with 2N HCl, brine, dried and evaporated to dryness to give oily residue. The crude product is then crystallized from ethanol to yield 2,6,6-trimethyl-4-(2-nitro-4-trifluoromethoxybenzoyl)-2H-1,2-oxazine-3,5(4H, 6H)-dione, m.p. 73-75.5°.

Proceeding analogously to Example 1 the following compounds of formula I are obtained.

TABLE A

Cpd	R_1	R_2	R_3	R_4	R	R_5	R_6	m.p.
1	CH ₃	CH ₃	CH ₃	H	NO ₂	4-OCF ₃	H	73-75.5°
2	CH ₃	CH ₃	CH ₃	H	Cl	4-OCHF ₂	H	95-97°

EXAMPLE 2

Preparation of 2-nitro-4-trifluoromethoxybenzonitrile

To a stirred solution of 64.30 g of 2-nitro-4-trifluoromethoxyaniline (Zhur. Obshchei. Khim 31, 915-24 (1961)) in 72 ml of concentrated hydrochloric acid and 190 ml of water, cooled to 0° is added dropwise over 35 min. a solution of 20.0 g of sodium nitrite in 75 ml of water. After stirring at 0°C for an additional 45 min., the diazonium salt solution is added dropwise, in portions, over 75 min. to a stirred solution of 82.69 g of potassium cyanide and 46.62 g of cupric sulfate in 400 ml of water at 60-65°C. The gray-greenish mixture is stirred and heated at 60-65°C for an additional 30 min and then allowed to cool to r.t. The mixture is filtered through celite and the precipitate is washed with dichloromethane (3 x 200 ml). The dichloromethane washings are used to extract the aqueous solution. The combined extracts are washed with water, brine, dried and evaporated to dryness to give an oily residue which is chromatographed on silica gel to give 31.44 g of 2-nitro-4-trifluoromethoxybenzonitrile.

EXAMPLE 3

Preparation of 2-nitro-4-trifluoromethoxy benzoic acid

A stirred solution of 40.96 g of 2-nitro-4-trifluorobenzonitrile in 90 ml of concentrated sulfuric acid and 125 ml of water is refluxed for 45 hrs. The reaction mixture is cooled and diluted with 200 ml of cold water. The aqueous supernatant is decanted from the brown crystalline gum. The crystalline gum is dissolved in ether and extracted with 0.5 N sodium hydroxide solution. The combined basic aqueous solution is cooled and acidified with concentrated hydrochloric acid and then extracted with ether. The combined extracts are dried and evaporated to dryness to give crystalline 2-nitro-4-trifluoromethoxybenzoic acid m.p. 119°C.

EXAMPLE 4

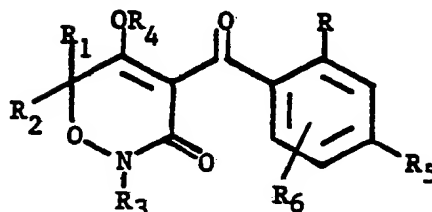
Preparation of 2,6,6-trimethyl-5-(2-nitro-4-trifluoromethoxybenzoyloxy)-6H-1,2-oxazine-3-one (Formula II $R_1=R_2=R_3=CH_3$; $R_4=R_5=H$; $R=NO_2$; $R_5=OCF_3$)

A stirred solution of 43.98 g of 2-nitro-4-trifluoromethoxybenzoic acid in 100 ml of thionyl chloride is refluxed for 2 hrs and then concentrated to dryness to give oily 2-nitro-4-trifluoromethoxybenzoyl chloride. To a stirred solution of 27.53 g of 2,6,6-trimethyl-2H-1,2-oxazine-3,5(4H, 6H)-dione and 35 ml (25/mm) of triethylamine in 290 ml of dichloromethane, cooled in an ice bath, under nitrogen, is added dropwise a solution of 2-nitro-4-trifluoromethoxybenzoyl chloride in 100 ml of dichloromethane. After stirring at 0°C at r.t. for 2 hrs., the reaction mixture is diluted with 150 ml of dichloromethane and the solution is washed with water, brine, dried and evaporated to dryness to give 2,6,6-trimethyl-5-(2-nitro-4-trifluoromethoxybenzoyloxy)-6H-1,2-oxazine-3-one.

10

WE CLAIM

1. A compound of formula I



I

wherein,

each of R_1 , R_2 and R_3 is independently hydrogen, C_{1-8} alkyl, carboxyl, C_{1-8} alkoxycarbonyl, phenyl or phenyl substituted by one to three groups as R, or R_1 and R_2 together form a C_{3-6} alkylene bridge
 R_4 is hydrogen, C_{1-8} alkyl, C_{1-8} alkylcarbonyl, C_{1-8} alkoxycarbonyl, $-C(O)NR_7R_8$, C_{1-8} alkylsulphonyl, $P(O)-(OR_9)_2$, $R_7P(O)-OR_9$, benzoyl or a cation;

R is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkoxy optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkylcarbonyl, C_{1-8} alkoxycarbonyl, NR_7R_8 , $O_nS(O)_{n'}R_{10}$, $NR_7SO_2R_8$, halogen, cyano or nitro;

R_5 is C_{1-8} alkoxy substituted by 1 to 6 halogen atoms;

R_6 is hydrogen or selected from the meanings given for R;

each of R_7 and R_8 is independently hydrogen or C_{1-8} alkyl;

R_9 is C_{1-8} alkyl;

R_{10} is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms;

n is 0 or 1;

n' is 0, 1 or 2;

provided that when R_1 , R_2 and R_3 are methyl, R_4 and R_6 are hydrogen and R is nitro, R_5 is not difluoromethoxy.

2. A compound according to Claim 1 wherein each of R_1 , R_2 , R_3 is selected from hydrogen or C_{1-4} alkyl;

R is selected from C_{1-4} alkyl optionally substituted with chloro, bromo, or fluoro, $-(O)_n-S(O)_{n'}-C_{1-4}$ alkyl, halogen or nitro;

R_5 is fluoroalkoxy;

R_6 is selected from hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, bromo, chloro;

R_4 is selected from H, C_{1-4} alkyl, C_{4-8} alkylcarbonyl, benzoyl, C_{1-4} alkylsulphonyl or a cation.

3. A compound according to Claim 2 wherein

each of R_1 , R_2 and R_3 is selected from H, C_{1-3} alkyl

R_4 is H;

R is selected from NO_2 , Cl, CF_3 .

4. A compound according to Claim 3 wherein R_1 , R_2 and R_3 are each methyl, R_4 and R_6 are each hydrogen, R is nitro and R_5 is OCF_3 .

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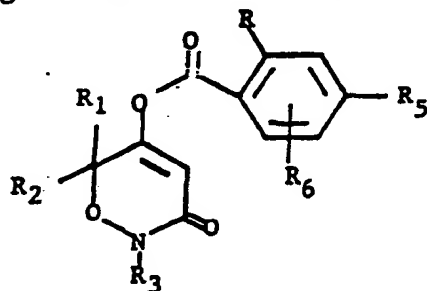
5. A pesticidal composition comprising the compound of formula I as defined in Claims 1-4, in association with an agriculturally acceptable carrier.

6. A method of controlling weeds comprising applying to the weeds or their locus herbicidally effective amount of a compound of formula I as defined in Claims 1-4.

7. A method of controlling acari comprising applying to the acari or their locus an acaricidally effective amount of a compound of formula I as defined in Claims 1-4.

8. A process for preparing a compound of formula I as defined in Claim 1 which comprises

a) rearranging an enol ester of formula (II)



II

wherein R_1 , R_2 , R_3 , R , R_5 and R_6 are as defined in claim 1 to give a compound of formula I wherein R_4 is H

b) when R_4 is other than hydrogen reacting a compound of formula I wherein R_4 is hydrogen with either

a) the group R_{40} -OH and a catalyst, or

b) the group R_{40} -Q and a moderate base, wherein Q is a halogen atom, to give a compound of formula I where R_{40} is the desired substituent.

9. 2-nitro-4-trifluoromethoxy benzoic acid.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 91/02014

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07D265/02; A01N43/72; C07C205/59

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C07D ;

A01N ;

C07C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 090 262 (STAUFFER CHEMICAL COMPANY) 5 October 1983 see claims ---	1-8
A	EP,A,0 186 117 (STAUFFER CHEMICAL COMPANY) 2 July 1986 cited in the application see claims ---	1,8
P,X	EP,A,0 394 889 (SANDOZ AG) 31 October 1990 see page 9, table A, Cpd. 22 and claims ---	1-8

¹⁰ Special categories of cited documents : ¹⁰¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance¹⁰ "E" earlier document but published on or after the international filing date¹⁰ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or other means¹⁰ "P" document published prior to the international filing date but later than the priority date claimed¹² "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹² "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹² "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹² "A" document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

15 JANUARY 1992

Date of Mailing of this International Search Report

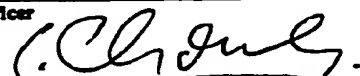
27. 01. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

CHOULY J.



**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9102014
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